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THE COMPOSITION OF EDIBLE BONE MEAL[1]

By J. C. BARTLET, CLEO COUTU, ETHEL LIST, and MARGARET WOOD

ABSTRACT

The composition of 16 samples of edible bone meal from three processors was determined. The average values obtained were calcium 33.0%, phosphorus 15.4%, total ash 87.9%, and moisture 1.46% with only a slight variation between samples. The fluoride content varied between 350 and 770 p.p.m. with an average of 572 p.p.m. The average zinc content was 129 p.p.m. and with one exception less than 10 p.p.m. of lead was present. Less than 10 p.p.m. of copper and 1 p.p.m. of arsenic was found. The average bacterial plate count of samples from two processors was less than 200 per gram; from a third processor 4000 per gram. *E. coli* was not found in any 10 gm. aliquot. The presence of anaerobic spore-forming thermophiles was insignificant.

INTRODUCTION

Edible bone meal has long been used as a source of calcium and phosphorus in baby foods and some enriched flours, and as a dietary supplement. However a review of the literature revealed very few figures for the composition of bone meal prepared for human consumption, neither was any indication of the bacterial content of the product recorded. The principal inorganic constituents of bone are calcium, phosphates, and carbonates, with small amounts of magnesium, sulphates, and fluorides also present. In addition trace amounts of lead, zinc, copper, and arsenic may be found.

The amount of fluorine in bone meal added to food has attained an added significance in recent years since the effect of fluorine in retarding dental caries has been demonstrated. The fluoridation of the water supply in many communities has followed the recognition of this fact. However, fluorine, if ingested in excessive amounts, can result in harmful effects, and therefore the fluorine content of foods is of considerable interest.

The concentration of fluorine in bone varies widely since it is related to the age (11) and diet of the animal (2). Values as high as 0.6 to 1.6% fluorine have been reported in the bones of English cattle suffering from fluorosis. This fluorosis was attributed to fluorspar, phosphatic rocks, and high fluoride clays in the pasture areas (2). Fluorosis has also been reported as occurring near aluminum factories using cryolite. Boddie (3) reports 0.30 to 1.25% fluorine in the bones of affected sheep. The literature concerning fluorine content of

normal bones is extensive and has been reviewed by Monier-Williams (7) and Sinclair (11). The range of values reported for beef bone from normal animals is from 100 to 1200 p.p.m. with most of the values falling in the range of 300 to 800 p.p.m. These values however do not indicate the amount of fluorine likely to be encountered in edible bone flour. Therefore this survey was conducted to determine the fluorine content and the percentage of other chemical constituents present in the bone meal intended for use in food products and pharmaceuticals.

The preparation of bone flour involves exacting treatment with steam under pressure. The product will, therefore, have been sterilized. Accordingly, any bacteria present in a sample in transit would be assumed to have gained access subsequent to processing. Accidental contamination by handling might include organisms of fecal origin. Similarly, dust or ineffectual cleansing of equipment would be expected to contribute thermoduric and thermophilic bacteria. Accordingly it was deemed desirable that any estimation of the bacteriological safety of edible bone flour should place emphasis on absence or low tolerance of fecal bacteria and of those organisms which are a major cause of spoilage in processed foods, namely, anaerobic thermophilic spore-forming species. This was particularly true since the product is largely used as an accessory ingredient in baby foods, also in certain pharmaceutical preparations and canned foods. Thus the product was examined for three microbial categories: standard plate count, presence of coliform bacteria, and the presence of anaerobic thermophilic spores.

ANALYTICAL METHODS

The following methods were employed in this survey.

Chemical Methods

Moisture

A weighed sample was oven-dried at 110°C. The loss in weight was taken as moisture.

Ash

A weighed sample was ignited overnight at 550°C. and the residue was taken as ash. Although it was not possible to obtain a perfectly white ash at this temperature, the ash percentage obtained by this method was reproducible. At higher temperatures partial loss of carbon dioxide from carbonates gave variable results. This ash was employed for the spectrographic determination of lead, zinc, and copper.

Calcium

The ignited sample was dissolved in dilute hydrochloric acid and an aliquot taken for analysis. The calcium was precipitated as the oxalate at pH 4, the precipitate dissolved in dilute sulphuric acid, and titrated with standard potassium permanganate (5).

Phosphorus

An aliquot of the ignited sample solution was used for the colorimetric determination of phosphorus by molybdenum blue with aminonaphtholsulphonic acid as reducing agent (10).

Lead, Zinc, and Copper

These elements were precipitated as sulphides with bismuth as a carrier and then determined spectrographically. The sulphides were mixed with graphite powder and arced with a d-c. arc at 6 amp. The intensity ratios of lines of lead, zinc, and copper to a bismuth line were calculated and the amount of each element was determined from standard curves.

Fluoride

The samples were ashed at 550°C. with calcium hydroxide added as a fixative. The ashed samples were dissolved in perchloric acid and the fluorine distilled as fluosilicic acid at 135°C. by the method of Willard and Winter (12). About 190 ml. of distillate was collected, neutralized with 0.1 N sodium hydroxide, and made slightly acid to phenolphthalein with 1N acetic acid. To a 10 ml. aliquot of the distillate, 10 ml. of alcohol was added and the solution was titrated with thorium nitrate using gallocyanine as the indicator (8). The titration was carried out in a test tube in an Evelyn Colorimeter employing a 620 mμ filter. Increments of 0.1 to 0.2 ml. thorium nitrate solution were added with stirring from a 5 ml. microburet. The transmission of the sample was measured after each addition. As the end point was approached, the increment added was reduced to 0.02 ml. The end point was considered to be the point at which the maximum transmission was first obtained. It was necessary to go past the end point and determine the exact volume required to reach this point by inspection of the readings. If the titration is carried out visually, the end point is obscured by the formation of a precipitate. This, however, does not interfere with the colorimetry when 250 μgm. or less is being titrated. The reproducibility of the titration is $\pm$ 0.02 ml. or $\pm$ 6 μgm. of fluorine at the 200 μgm. level. The reproducibility drops off sharply above 250 μgm.

The reagents were made up exactly as described by Rickson (8), but the amount of thorium nitrate needed for a given amount of fluoride was only approximately one-third of that used by Rickson. All reagents were checked and no reason for the discrepancy was found. It was noted that the gallocyanine indicator prepared with 50% ethanol was more stable than in aqueous solution.

Arsenic

The sample was ashed at 550°C. with magnesium nitrate as a fixative and the arsenic determined by the Gutzeit method of the A.O.A.C. paragraphs 24.1 to 24.5 (1).

Bacteriological Methods
Standard Plate Count

An aliquot of 10 gm. of bone flour was suspended in 90 ml. of sterile water and shaken in a reciprocating mechanical shaker for five minutes. Appropriate dilutions were prepared from this suspension using 10 ml. aliquots. With Difco nutrient agar as the medium, plates were poured in triplicate from each dilution using 1-ml. specimens and incubated for 48 hr. at 37°C. The plate count was estimated from the dilution containing the most favorable number of colonies, viz., approaching from 30 to 200 colonies per plate.

The Determination of Coliform Bacteria

Dilutions were prepared as for the plate count. From each dilution, 1-ml. aliquots were introduced into each of five tubes of Difco lactose broth containing gas vials. The presence of coliforms in each tube, as indicated by production of gas after 48 hr. at 37°C. was confirmed using plates of Endo's agar. "Most probable numbers" were estimated from standard M.P.N. tables.

The Determination of Anaerobic Thermophilic Spores

The method used for anaerobic thermophilic spores was essentially that of the A.O.A.C. as used for Sugar or Starch, Paragraphs 36.12 to 36.16 (1).

RESULTS AND DISCUSSION

Chemical Composition

Table I gives the composition of 16 representative samples from the three processors. The percentages of calcium and phosphorus show little significant difference between samples from the different producers. Since all the samples were made from beef bone, this constancy of composition was to be expected. The fluoride content of all the samples is appreciable, varying from 350 p.p.m. to 770 p.p.m. Samples from Processor *A* contained the smallest amount of fluorine with an average of 458 p.p.m. while the samples supplied by Processor *C* had the highest average of 693 p.p.m.

The zinc content of the bone meal is virtually the same for all samples and it is probable that this amount of zinc was present in the original bones. Hove *et al.*

TABLE I
THE COMPOSITION OF EDIBLE BONE MEAL

Processor	Moisture, %	Ash, %	Ca, %	P, %	F, p.p.m.	Zn, p.p.m.	Pb, p.p.m.
A	1.74	88.5	33.6	15.6	490	130	4
	1.68	88.4	33.7	14.8	470	130	4
	1.72	88.4	33.9	15.6	530	125	3
	1.68	88.5	33.9	16.0	420	150	4
	1.68	88.5	33.5	15.9	380	125	3
Average	1.70	88.5	33.7	15.6	458	132	4
B	1.94	89.1	33.2	15.6	500	150	8
	1.92	88.4	32.7	15.3	480	130	6
	1.90	87.8	33.0	15.2	630	140	6
	1.06	88.8	33.1	15.7	770	130	6
	0.91	88.1	33.2	15.6	660	125	4
	0.82	88.3	33.0	15.3	710	125	6
	0.79	88.5	31.5	14.5	350	110	4
	0.93	88.2	32.8	15.5	690	130	20
Average	1.28	88.4	32.8	15.3	599	130	8
C	1.58	86.5	32.5	15.3	700	125	7
	1.59	85.3	32.8	15.3	670	125	6
	1.41	85.0	32.2	15.3	710	120	7
Average	1.53	85.6	32.5	15.3	693	123	7

(4) reported 92 p.p.m. zinc in bones of rats fed on a diet containing an adequate supply of zinc and Mawson and Fischer (6) reported 233 p.p.m. in the tibia of a rat. However, no figures were found for zinc in beef bone. With the exception of the one sample from Processor *B* no sample contained more than 10 p.p.m. lead. In all cases the amount of lead found was probably present in the original bones since this element is known to accumulate in bones. Human bones have been reported containing as much as 140 p.p.m. (9). Copper was found to be less than 10 p.p.m. in all samples and arsenic less than 1 p.p.m. in every case.

Microbial Content

The numbers of bacteria of the three test categories, present in 37 samples of edible bone flour, are presented in Table II. It will be noted that the plate count

TABLE II

THE DETERMINATION OF BACTERIA IN EDIBLE BONE FLOUR

Processor	Sample		Bacterial plate count expressed as number per gm.	Thermophilic anaerobic spores	Coliforms
	Lot	Aliquot			
A	1		130	0	0
	2		200	0	0
	3		50	0	0
	4		120	0	0
	5		170	0	0
B	6	*a*	340	0	0
		b	230	0	0
		c	230	0	0
	7	*a*	50	0	0
		b	70	0	0
		c	30	0	0
	8	*a*	40	0	0
		b	20	0	0
		c	200	0	0
	9	*a*	230	0	0
		b	240	0	0
		c	70	0	0
	10	*a*	180	0	0
		b	100	1.5 per gm.	0
		c	580	0	0
	11	*a*	570	1.5 per gm.	0
		b	440	0	0
		c	970	0	0
	12		40	0	0
	13		120	0	0
	14		90	0	0
	15		110	0	0
	16		80	0	0
	17		20	0	0
	18		40	0	0
	19		10	0	0
	20		20	0	0
	21		20	0	0
	22		40	0	0
C	23		2000	0	0
	24		4000	0	0
	25		7000	0	0

is less than 1000 per gram in all instances except those of Processor C. The average plate count for Processors A and B is less than 200.

Coliforms were not found in any 10 gm. sample. Anaerobic thermophilic spores were of no practical significance.

If for any reason it were desirable to determine whether the plate count of a given specimen significantly exceeded any specified bacteriological standard, then allowance for the inexactitude of the method and for sampling variations will be provided by the formula

$$T = (\sqrt{C} + 2\sigma)^2$$

where T = tolerated count, C = count for the weight of the sample on the basis of the specified standard (i.e. if standard count is 1000 per gram, and a 0.1 gm. sample is counted, then $C = 100$), σ = standard deviation of the square roots of the counts of multiple samples from the same production unit. Then if the count of a sample exceeds the calculated value of T, the bacterial content of the sample is significantly higher than the specified standard.

ACKNOWLEDGMENTS

REFERENCES

1. Assoc. Official Agr. Chemists. Official methods of analysis, 7th ed. A.O.A.C. 1950.
2. BLAKEMORE, F. Proc. Nutrition Soc. (Engl. and Scot.), 1 : 211-215. 1944.
3. BODDIE, C. F. Proc. Nutrition Soc. (Engl. and Scot.), 3 : 94-97. 1945.
4. HOVE, E., ELVEHJEM, C. A., and HART, E. B. Am. J. Physiol. 124 : 750-758. 1938.
5. KOLTHOFF, I. M. and SANDELL, E. B. Textbook of quantitative inorganic analysis. Revised edition. Macmillan Co., New York. 1943. pp. 345-360.
6. MAWSON, C. A. and FISCHER, M. I. Nature, 167 : 859. 1951.
7. MONIER-WILLIAMS, G. W. Trace elements in foods. Chapman and Hall Ltd., London. 1949. pp. 348-352.
8. RICKSON, J. B. Analyst, 75 : 84-91. 1950.
9. ROCHE-LYNCHE, G., SLATER, R. H., and OSLER, T. G. Analyst, 59 : 787-803. 1934.
10. SHERMAN, MILDRED S. Ind. Eng. Chem., Anal. Ed. 14 : 182-185. 1942.
11. SINCLAIR, MISS K. J. Med. Research Council Mem. No. 22, Ind. Fluorosis, pp. 97-105. 1949.
12. WILLARD, H. H. and WINTER, O. B. Ind. Eng. Chem., Anal. Ed. 5 : 7-10. 1933.

OXIDATION OF PETROLEUM RESIDUES[1]

By W. Graham,[2] W. J. G. Cudmore,[3] and R. D. Heyding[4]

ABSTRACT

The oxidation of a steam reduced crude and a cracked petroleum residue by air and oxygen blowing at 200°C. has been investigated. The change in the quantities of oils, resins, and asphaltenes with oxidation has been determined, as well as the oxygen content of these fractions. The oxygen absorbed by the residue was found to be small compared with the oxygen consumed in the formation of water and carbon dioxide. The relative rates of formation of the asphalt fractions are discussed.

INTRODUCTION

It is well known that air blowing of petroleum residues produces hard, short asphalts, with the evolution of volatile oils, water, and carbon dioxide. It has been shown that the oxidation is accompanied by an increase in the quantity of asphaltenes in the petroleum residue at the expense of the oils and resins (4, 5). An increase in the mean molecular weight of all three fractions was observed, and the over-all reaction is considered to be one of slow polymerization of the oils and resins to asphaltenes.

Although the quantities of water and carbon dioxide evolved during the oxidation of tar oils have been determined (2), no analogous study of the oxidation of petroleum residues or asphalt has been reported. The present investigation was undertaken to determine the relative quantities of water and carbon dioxide evolved, as well as the total oxygen consumed, with respect to the conversion of oils and resins to asphaltenes during the oxidation of petroleum residues.

EXPERIMENTAL PROCEDURE

Blowing of Petroleum Residues

Steam refined Lloydminster reduced crude, and cracked stock from Leduc crude, both commercially prepared, were selected for the blowing experiments. The reduced crude had a Saybolt Furol viscosity of 152 sec. at 130°F. and the cracked stock, 74.1 sec. at 130°F. These residues were blown with oxygen, with nitrogen, and with air, at a moderate temperature and a low blowing rate to facilitate the recovery of distilled oils, water, and carbon dioxide.

The blowing apparatus is illustrated in Fig. 1. Carbon dioxide, water, and extraneous matter were removed from the incoming gases with sulphuric acid (A), calcium chloride (B), soda lime (C), and dehydrite (D). For nitrogen blowing, hot copper turnings at 300°-600°C. preceded the purification train to

remove traces of oxygen (not shown in Fig. 1). The reaction vessel (E) was a three-necked 500 ml. round-bottom flask fitted with a thermometer and a five-holed bubbler for dispersion of the gas stream. Heat was supplied by a Glas-col mantle controlled manually by a Variac. The tower (F) lightly packed with glass wool, served to trap the majority of the distilled oils, the remainder being
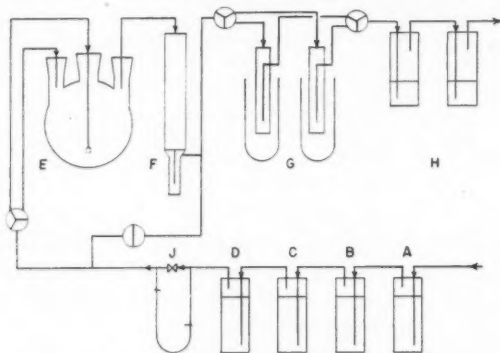
FIG. 1.   Asphalt blowing apparatus.

trapped along with the water evolved in the dry ice – acetone cooled traps (G). During experiments on the reduced crude, saturated solutions of barium hydroxide (H) were employed to recover the carbon dioxide evolved. These were replaced by ascarite absorption tubes for experiments on the cracked stock. Gas flow rates were measured by a capillary flowmeter (J).

Nitrogen and oxygen were supplied to the system from high pressure cylinders and the flow rate controlled by diaphragm valves. In air blowing the reduced crude, air was drawn through the system by means of a rotary oil pump, while compressed air, controlled by a low pressure diaphragm valve, was used in blowing the cracked stock.

The tared reaction flask was charged with 200 ± 1 gm. of petroleum residue, weighed to the nearest 0.1 gm. The temperature was brought to 200° ± 3°C. as quickly as possible (about 20 min.), with the system open to the atmosphere until 100°C. was attained, at which time blowing was commenced to prevent spot heating in the flask. The blowing rate was 1.5 ml. of gas per gram per minute at room temperature and pressure. At the completion of the blowing period, heat was removed and the reaction flask flushed with nitrogen for one hour to ensure removal of all water, carbon dioxide, and distilled oil. The flask was weighed and the residue removed while still warm.

The distilled oils were washed from the scrubbing tower with 250 ml. of benzene, the solvent removed by distillation, and the oils dried at 110°C. The water and oil in the cold traps were separated by means of a capillary separatory funnel and weighed. When barium hydroxide traps were used, the precipitate was recovered by filtration, washed, and dried in a vacuum desiccator. A blank was necessary to correct for the precipitate formed during filtration.

RESULTS

Representative results obtained in the blowing experiments are given in Table I and are expressed in grams of product per hundred grams of petroleum residue as charged. In duplicate experiments, the variation in quantity of water recovered was never greater than 10%, of distilled oil 15%, and of blown residue, 2%.

TABLE I

BLOWING OF PETROLEUM RESIDUES

Temperature, $200° \pm 3°C$.
Gas flow, 1.5 ml. gm.$^{-1}$ min.$^{-1}$ (20°C., 720 mm.)
Basis, 100 gm. of petroleum residue as charged

Blowing medium	Time, hr.	Distilled oil, gm.	Water, gm.	Carbon dioxide, gm.	Blown residue, gm.
Lloydminster reduced crude					
Air	10	4.45	0.54		95.2
	20	6.43	1.05	0.072	94.1
	30	9.29	1.38		90.5
	40	11.5	1.89	0.146	88.3
	50	12.9	2.25		87.3
	60	13.1	2.45	0.175	87.5
Oxygen	10	4.85	2.28	0.100	94.9
	15	6.08	2.65	0.135	93.8
	20	6.72	3.31	0.171	93.3
Nitrogen	20	6.28	0.05	0.000	93.3
	60	11.2	0.05	0.000	87.6
	120	19.0	0.05	0.000	80.9
Leduc cracked stock					
Air	10	1.64	1.16		98.1
	20	3.11	2.12		96.9
	30	5.56	3.07		93.9
	41	6.66	3.69		93.4
	50	7.23	4.44		92.9
	60	12.8	4.70		89.0
Nitrogen	22	3.27	0.09		95.7
	42	6.78	0.13		92.5
	63	8.44	0.15		90.6

In calculating the quantity of carbon dioxide evolved during the oxidation of the reduced crude, it was assumed that the precipitates from the barium hydroxide traps were essentially pure barium carbonate. However, it was observed that a solution of the precipitate in dilute acid reduced small quantities of permanganate, although anions other than carbonate could not be detected by standard qualitative analysis. The increase in weight of the ascarite absorption tubes has not been included in Table I, since it was observed that traces of distilled oil were deposited on the absorbent.

The physical properties of the blown residues, determined according to A.S.T.M. procedures, are given in Table II.

TABLE II

PHYSICAL PROPERTIES OF BLOWN RESIDUES

Blowing medium	Time, hr.	Penetration, 100 gm., 5 sec.		Ductility at 77°C., cm.
		32°F.	77°F.	
Lloydminster reduced crude Nitrogen	120	85		
Air	10	182		
	20	95		
	30		160	110
	40		72	44.8
	50		43	8.6
	60		31	5.5
Oxygen	10		113	17.5
	15		62	6.3
	20		33	2.9
Leduc cracked stock Air	41		105	
	50		35	
	60		8	

Fractionation of Blown Residues

The oil, resin, and asphaltene contents of the petroleum residues and of the blown residues were determined by the method described by Hubbard and Stanfield (3). In this method, the asphaltenes are defined as that portion of the asphalt which is not soluble in n-pentane. The soluble portion (the malthenes) is distributed on anhydrous alumina, and the fraction which is desorbed with n-pentane in one hour in a constant temperature extractor (3) is defined as the oils. The remainder (the resins) is desorbed by a methanol–benzene solvent pair.

In the present investigation, the pure n-pentane suggested by Hubbard and Stanfield was replaced by technical pentane (b.p. 33°-36°C.). The absorbent was Alcoa activated alumina, screened to 100-200 mesh, and prepared by heating at 700°C. for two hours and cooling in a vacuum desiccator. Extraction of the oils from the resins was effected at 25°C. The precision in analysis was greater than 1% for all three fractions, and the average total loss was less than 0.5%. The results of the fractionations are given in Table III.

The oils contained in the blown reduced crude were similar to, although more viscous than, the distilled oils and showed no appreciable color change due to blowing. The oil fraction recovered from the blown cracked stock, however, was a low melting wax, which changed color from orange-yellow to pale yellow on blowing. The resins from the reduced crude and cracked stock were, respectively, tacky liquids and solids at room temperature. The asphaltenes recovered from all residues were brownish-black solids.

TABLE III
OIL, RESIN, AND ASPHALTENE CONTENT OF
BLOWN PETROLEUM RESIDUES

Blowing medium	Time, hr.	Oils, %	Resins, %	Asphaltenes, %
Lloydminster reduced crude				
Original residue		46.9	37.7	15.3
Air	20	40.2	34.1	25.1
	40	35.3	31.7	32.9
	60	31.9	28.6	39.0
Oxygen	10	37.4	33.1	29.3
	15	35.3	29.9	34.1
	20	33.4	28.9	37.5
Nitrogen	60	40.6	40.5	18.0
	120	36.7	43.1	20.1
Leduc cracked stock				
Original residue		67.0	23.2	8.6
Air	10	59.5	20.5	19.0
	20	52.9	20.4	26.7
	30	48.4	18.6	32.0
	41	45.1	18.3	36.4
	50	43.6	16.6	39.7
Nitrogen	22	64.3	24.2	10.6
	42	61.7	24.1	13.4
	63	61.5	24.6	14.4

Oxygen Content of Oils, Resins, and Asphaltenes

The oxygen contents of the hydrocarbon fractions were determined by pyrolysis of the sample in an atmosphere of nitrogen and conversion of the oxides to carbon monoxide with hot carbon (1100°C.). The monoxide was subsequently oxidized to carbon dioxide with iodine pentoxide with the liberation of free iodine, which was collected and titrated with standard sodium thiosulphate. This method was first described by Schütz (6) and later modified by Unterzaucher (7). The procedure was checked by analyzing six pure organic compounds ranging in oxygen content from 6% to 26%. Although it was necessary to correct for large variable blank values (1, 8), the analysis was found to be accurate within ± 1%.

The oxygen contents of the oils, resins, and asphaltenes are given in Table IV. The oxygen contents of the oils distilled from the reduced crude were not determined.

DISCUSSION OF RESULTS

The results of the fractionation and oxygen determinations have been expressed in Table V in grams per hundred grams of petroleum residue as charged. It has been assumed that the oils distilled from the reduced crude contained the same quantity of oxygen as the oil remaining in the residue.

TABLE IV

OXYGEN CONTENT OF OILS, RESINS, AND ASPHALTENES,
% OXYGEN BY WEIGHT

Blowing medium	Time, hr.	Distilled oils	Oils	Resins	Asphaltenes
Lloydminster reduced crude					
Original residue			0.42	1.29	2.89
Air	20	—	0.35	1.38	2.76
	40	—	0.35	1.49	2.59
	60	—	0.32	1.51	2.63
Oxygen	10	—	0.44	1.52	2.55
	15	—	0.35	1.57	2.86
	20	—	0.37	1.86	2.72
Nitrogen	60	—	0.49	1.19	—
	120	—	0.49	1.11	2.75
Leduc cracked stock					
Original residue			0.21	1.50	1.43
Air	10	0.57	0.43	1.83	1.74
	20	0.45	0.27	2.08	2.32
	30	0.43	0.22	1.70	2.69
	41	0.39	0.24	1.80	2.89
	50	0.39	0.30	2.16	2.98
Nitrogen	22	0.31	0.24	1.40	1.23
	42	0.34	0.22	1.36	1.06
	63	0.37	0.20	1.26	1.09

The quantity of oils distilled from each crude was found to be essentially independent of the blowing medium employed. Blowing with nitrogen had little effect on the reduced crude other than on its distillation, while blowing of the cracked stock with nitrogen resulted in a small but significant decrease in resins and total oils, and an increase in asphaltene content. This is taken to indicate the presence of components in the cracked stock capable of polymerization by heat and agitation in the absence of oxygen.

As had been shown previously, air oxidation of both crudes increased the quantity of asphaltenes in the residue at the expense of the oils and resins.

Oxidation of the reduced crude did not result in an appreciable change in the oxygen content of either the oils or the asphaltenes, although the oxygen content of the resins increased appreciably (Table IV). Thus if oxygen was retained by particular oil molecules, these must have been converted to resins or asphaltenes. The increased oxygen content of the resins may be attributed either to the formation of oxygen rich resins from the oil fractions or to the oxidation of the resins themselves. The probability of oxygen attacking the asphaltene molecules is decreased by the resins surrounding the asphaltene micelle, consequently the asphaltenes formed at the expense of the oils and resins would appear to have essentially the same oxygen content as the original asphaltenes.

The oxygen content of the resins and oils of the cracked residue increased sharply during the early stages of air blowing, decreased to a minimum value,

TABLE V

Blowing agent	Time, hr.	Petroleum fractions, (gm./100 gm. residue charged)						Oxygen content, (gm./100 gm. residue charged)						Oxygen as:		Total oxygen consumed
		Dist. oils	Oils	Total oils	Resins	Asphalt-enes	Total fractions	Dist. oils	Oils	Resins	Asphalt-enes	Total	Inc.	H₂O	CO₂	
Lloydminster reduced crude																
Original			46.9	46.9	37.7	15.3	99.9		0.20	0.49	0.44	1.13				
Air	20	6.4	37.8	44.2	32.1	23.6	99.9		0.15	0.44	0.65	1.24	0.11	0.87	0.05	1.03
	40	11.5	30.8	42.3	27.6	28.7	97.6		0.15	0.41	0.74	1.30	0.17	1.68	0.11	1.96
	60	13.1	27.9	41.0	25.0	34.1	100.1		0.13	0.37	0.89	1.39	0.26	2.18	0.13	2.57
Oxygen	10	4.9	36.5	41.4	31.4	27.8	100.6		0.18	0.48	0.71	1.37	0.24	2.03	0.07	2.34
	15	6.1	33.1	39.2	28.0	32.0	99.2		0.14	0.44	0.91	1.49	0.36	2.35	0.10	2.81
	20	6.7	31.2	37.9	27.9	35.0	100.8		0.14	0.52	0.95	1.61	0.48	2.95	0.12	3.55
Nitrogen	60	11.2	36.6	47.8	36.5	15.8	100.1		0.23	0.47	0.43	1.13	0.00	0.05	0.00	
	120	19.0	29.7	48.7	34.9	16.3	99.9		0.24	0.42	0.45	1.13	0.00	0.05	0.00	
Leduc cracked Stock																
Original			66.6	66.6	23.3	8.4	98.3		0.14	0.35	0.12	0.61				
Air	10	1.7	58.1	59.8	21.7	18.6	100.2	0.01	0.25	0.40	0.32	0.98	0.37	1.00	—	1.36
	20	3.2	51.2	54.4	20.1	25.7	100.2	0.01	0.14	0.42	0.59	1.16	0.55	1.88	—	2.43
	30	5.7	45.9	51.6	18.4	30.4	99.4	0.02	0.10	0.31	0.82	1.25	0.64	2.67	—	3.31
	41	6.9	42.1	49.0	16.6	33.9	99.5	0.02	0.10	0.30	0.98	1.40	0.79	3.38	—	4.17
	50	7.2	39.9	47.1	15.1	36.0	98.2	0.03	0.12	0.33	1.07	1.55	0.94	3.87	—	4.81
Nitrogen	22	3.5	62.1	65.6	23.0	10.3	98.9	0.01	0.15	0.32	0.13	0.61	0.00	0.05	—	
	42	7.0	58.1	65.1	22.6	11.8	99.5	0.02	0.13	0.31	0.13	0.59	−0.02	0.11	—	
	63	8.7	53.8	62.5	22.3	13.7	98.5	0.04	0.11	0.28	0.15	0.58	−0.03	0.16	—	

and increased slowly as oxidation proceeded. The immediate increase indicates the presence of compounds in the cracked stock capable of forming oxygen rich products which ultimately decomposed or were further oxidized to resins and asphaltenes.   A second and slower reaction, also involving the inclusion of oxygen but as relatively stable products, could account for the increase in oxygen content during the latter stages of oxidation.

Unlike the reduced crude asphaltenes, the cracked stock asphaltenes doubled in oxygen content per unit weight over the blowing period. If the original asphaltenes were not appreciably oxidized, this increase must represent relatively high oxygen content in the asphaltenes formed during the reaction.

The difference in the chemical nature of the two residues is further indicated by the rates of change in the quantities of the three fractions with oxidation, these rates being greater for the cracked stock. Furthermore, it is evident in Fig. 2 that the reduced crude resins were more susceptible to oxidation than the
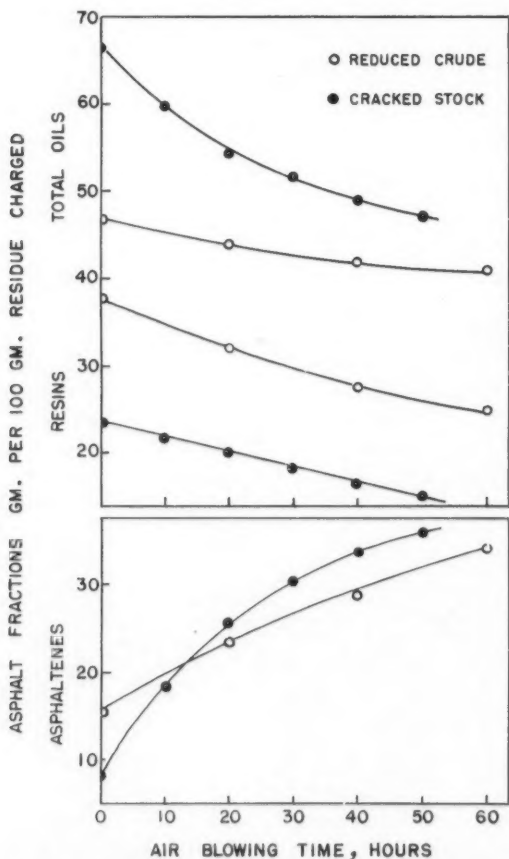

FIG. 2.   Change in oil, resin, and asphaltene content on air blowing.

corresponding oils, while the cracked stock oils disappeared more rapidly than the corresponding resins. Finally, the total oxygen consumption by the cracked residue exceeded that of the steam reduced residue by a factor of two (Fig. 3). These comparisons are necessarily qualitative since the two residues were not obtained from the same crude.
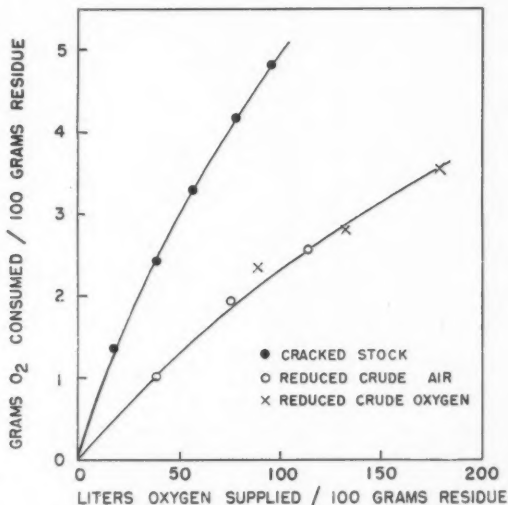

FIG. 3.   Total oxygen consumed per liter of oxygen supplied.

The oxygen consumed per mole of oxygen supplied to the reduced crude appeared to be independent of the concentration of oxygen in the blowing medium (Fig. 3), and further, the same relative proportions of water, carbon dioxide, and absorbed oxygen were obtained on both air and oxygen blowing. On the other hand, the rates of conversion of oils and resins to asphaltenes per mole of oxygen supplied were not found to be identical, but somewhat less on oxygen blowing than on air blowing. The velocities of polymerization reactions must therefore have been slower than oxidation reactions.

In comparing the quantities of oxygen evolved as water to the total oxygen consumed, it is evident that the primary reactions in both residues involved dehydrogenation. The marked physical changes accompanying the oxidation of asphalt under the conditions employed in this investigation may therefore be attributed to dehydrogenation and polymerization of particular asphalt molecules.

ACKNOWLEDGMENTS

REFERENCES

1. ALUISE, V. A., BECKER, W. W., HALL, R. T., and STAATS, F. C.   Anal. Chem. 19 : 347-351. 1947.
2. DICKINSON, E. J. and NICHOLAS, J. H.   Road Research, Tech. Paper No. 16, Dept. Sci. Ind. Research, London. 1949.
3. HUBBARD, R. L. and STANFIELD, K. E.   Anal. Chem. 20 : 460-465.   1948.
4. KAMPTNER, H. and MASS, W.   Asphalt u. Teer Strassenbautech. 38 : 679-684.   1938.
5. KATZ, D. L. and BEU, K. E.   Ind. Eng. Chem. 37 : 195-200.   1945.
6. SCHUTZ, M.   Z. anal. Chem. 118 : 245-258.   1939.
7. UNTERZAUCHER, J.   Ber. 72 : 391-404.   1940.
8. WALTON, W. W., McCULLOCH, F. W., and SMITH, W. H.   J. Research Natl. Bur. Standards, 40 : 443-447.   1948.

A TRANSIENT HEAT FLOW METHOD OF DETERMINING THERMAL CONDUCTIVITY: APPLICATION TO INSULATING MATERIALS[1]

By C. P. LENTZ[2]

ABSTRACT

When the line heat source was incorporated in a probe of a form considered suitable for use in insulating materials, results were found to be highly dependent on heat conduction through power and thermocouple leads, and on other factors in probe construction. Conductivities measured in rock wool (10 lb. per cu. ft.) were from 10% to 15% lower than accepted hot plate values, except when heat loss through end leads introduced a compensating error. Results from four tests under similar conditions agreed within a ± 3% range.

An unenclosed wire heater gave good results with granulated and blanket rock wool, silica aero-gel, and slab cork. A heater wire of very small diameter (0.01 in.) had to be used with insulation of low density (2 lb. per cu. ft.). Conductivities obtained varied linearly with heater current. There was no significant difference between results with the heater wire in horizontal and vertical positions. Results from four unenclosed wire heater tests under similar conditions fell within a ± 1.5% range.

INTRODUCTION

The line source transient heat flow method for thermal conductivity determination, originally developed for use with liquids, was based on an empirical equation. A more recent paper (6) contains a theoretical development. At this university, difficulty in measuring the thermal conductivity of soils led to interest in the method, and an instrument called a probe was developed for use in soils (1). The probe is essentially a straight wire heater enclosed in a metal tube.

It appeared that if this instrument could be adapted for use with thermal insulating materials, it would have many advantages over the hot plate method. The apparatus would be portable, relatively inexpensive, and its use would be much less time consuming. Further, the short duration of tests with the transient heat flow method might minimize error due to moisture migration in the test sample.

The purpose of this investigation was to determine some of the characteristics of the line source transient heat flow method for measuring thermal conductivity when applied to insulating materials.

THEORY

The line source transient heat flow method of thermal conductivity determination is based on the relation between thermal conductivity and the temperature rise in an infinite homogeneous medium caused by a line heat source of

constant strength. If the initial temperature of the medium is uniform, the temperature rise at a point at a distance r from the line source, at time t, is given by the following equation $(1, 2)$:

$$(1) \qquad \theta = \frac{q}{2\pi k} \int_{rn}^{\infty} \frac{e^{-\beta^2}}{\beta} d\beta = \frac{q}{2\pi k} [I(rn)],$$

where θ = temperature rise above initial temperature, °F.

q = heat units released per unit time per unit length of line source, B.t.u. per hr. per ft.

k = thermal conductivity, B.t.u. per hr. per ft. per deg. F.

r = distance from line source, ft.

$n = 1/2\sqrt{at}$

a = diffusivity, sq. ft. per hr.

t = time from start of heat flow, hr.

$\beta = r/\sqrt{4a(t-\tau)}$

$$(2) \qquad \text{and } I(rn) = C - \log_e(rn) + \frac{(rn)^2}{2} - \frac{(rn)^4}{8} + \ldots$$

If rn is sufficiently small,

$$I(rn) = C - \log_e(rn) \text{ and } \theta = \frac{q}{2\pi k} [C - \log_e(rn)].$$

The temperature rise between times t_1 and t_2 is then

$$(3) \qquad \theta_2 - \theta_1 = \frac{q}{4\pi k} \log_e \left(\frac{t_2}{t_1}\right).$$

In determining thermal conductivity by the transient heat flow method, θ, t, and q are measured and k is calculated from Equation (3).

In deriving Equation (1) an ideal line heat source of infinite length in an infinite medium is assumed whereas, in practice, the sample is of finite size, the heat source of finite length, and the mass and radius of the heat source are not zero. In addition, all the terms of the I series, except the first two, were dropped to obtain an equation in which a and r do not appear. These departures from ideal conditions have been analyzed in detail by Van der Held (6), but, since the conditions of his experiments were not the same as the conditions of the experiments reported here, the effect of these departures is reviewed briefly.

1. *Terms Dropped in I(x) Series*

The error caused by dropping terms in the $I(x)$ series can be shown to be negligible for the conditions of the experiments reported here.

2. *Finite Length of Heat Source*

The finite length of the heater introduces two errors, one due to distortion of the radial heat field, and the other due to heat conduction along the heater. While Van der Held shows the first of these to be negligible for conditions similar to those in this investigation, his equation for the second indicates the possibility of large error unless the heat source is of small enough diameter and great enough length.

3. *Finite Size of Sample*

Calculation shows that the finite size of samples of the type used in this investigation causes negligible error if the samples are six or more inches in diameter.

4. *Finite Size and Thermal Properties of the Heat Source*

This is a most important source of error and one for which Van der Held devised a correction. He derived an equation for the temperature field produced by an actual heat source, plotted the temperature given by this equation against time, and compared the resulting curve to the curve given by Equation (3). The two curves were similar in shape but displaced from each other by an almost constant time. From this almost constant displacement, Van der Held concluded that Equation (3) would describe the temperature field produced by an actual heat source if a corrected time were used. The time correction, (t_0), was determined from experimental results in the following way: the derivative of Equation (3) with $(t + t_0)$ substituted for t is

$$(4) \qquad \frac{d\theta}{dt} = \frac{q}{4\pi k}(t + t_0)^{-1} \text{ or } \frac{dt}{d\theta} = \frac{4\pi k}{q}(t + t_0) \ .$$

When $dt/d\theta$ is plotted against t, a straight line of slope $4\pi k/q$ with $t = -t_0$ at $dt/d\theta = 0$ is obtained. This t_0 is the required correction. Fig. 2, A shows the curves obtained in a typical test: t_0 in this case was -12 sec.

EQUIPMENT AND PROCEDURE

The probe form of the instrument, as proposed by Hooper and Lepper (1) was used in some of the tests. In it, the heater wire is enclosed in an aluminum tube of small diameter, as shown schematically in Fig. 1, A, providing a more convenient arrangement than the unenclosed heater wires used in other tests.

Fig. 1, B shows schematically the electric heater, and thermocouple for temperature measurement, with the auxiliary equipment consisting of constant-voltage, direct-current source, current measuring device, and potentiometer for measurement of thermocouple e.m.f.

Constantan wire was used for the heaters in all cases since it exhibits little change in resistance with change in temperature. The size of the wire used in most tests was No. 24. B & S gauge (.02 in.) although some were made using No. 30 B & S gauge (.01 in.).

Two six-volt storage batteries in parallel were used to supply heater current. A variable series resistance was used to adjust the current, which did not vary more than 0.5% during any experiment. A potentiometer was used across a standard shunt to measure current flow. The sensitivity of the potentiometer was 0.02 mv., which corresponded to 0.1% of the current flow in most of the experiments.

The temperature at the mid-point of the heater was measured with a 30 B and S gauge copper–constantan thermocouple in all experiments. The sensitivity of the potentiometer used was 0.0002 mv., which corresponds to 0.1°F. The
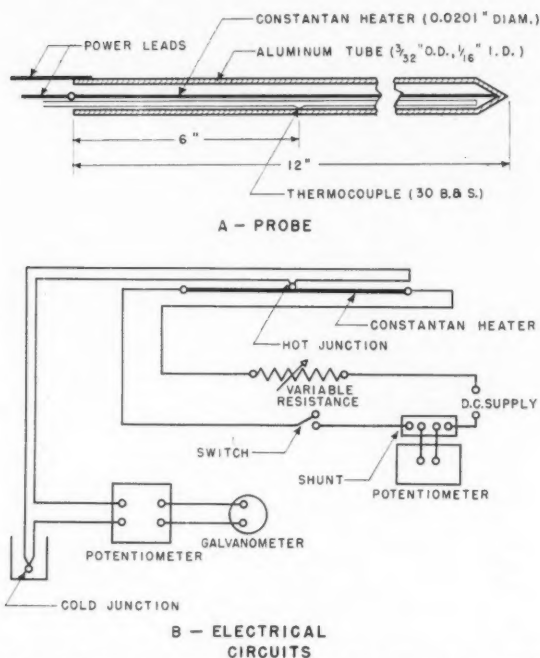
FIG.1. Schematic diagram of probe and electrical circuits.

sensitivity of the galvanometer used with the potentiometer was 0.003 μa. per mm. at 1 meter.

A stop watch was used to measure the time from the start of current flow with an accuracy of $\pm$ one second.

The first step in calculating the result of a test was to plot the temperature rise above the initial temperature against time (Fig. 3, A). Equation (4) shows that if $dt/d\theta$ is plotted against t a straight line having a slope of $4\pi k/q$ should be obtained. When $dt/d\theta = 0$, $t = -t_0$; in other words, the curve will intersect the t axis at $-t_0$. Values of $dt/d\theta$ were obtained by drawing tangents to the time–temperature rise curve and $dt/d\theta$ was then plotted against t to obtain t_0 (Fig. 3, A).

The thermal conductivity of the specimen was then calculated from Equation (3), using times corrected by the amount t_0. It was found that, in some tests, the value of k obtained in the calculation varied by as much as 5%, depending on the particular values of t_1 and t_2 used. For this reason k was calculated for a number of different values of t_1 and t_2, and the average was used. The same procedure was followed for all tests.

Although moisture content in the test samples was not controlled it was assumed that moisture effects could be neglected since most of the samples were nonhygroscopic and the relative humidity was low.

1. *Preliminary Tests*

The first series of tests was made with an unenclosed heater wire in an attempt to determine the limitations of the equipment, and in particular to provide information on the effect of thermocouple position, and the duration of the test.

The same undisturbed sample of a granular type of rock wool was used for all the tests. The granules or balls were about 0.5 in. in diameter. The sample was packed to a density of 10 lb. per cu. ft. to ensure a certain degree of homogeneity. The conductivity of the sample material as given by hot plate tests was 0.28 B.t.u. per hr. sq. ft. deg. F. per in.

The heater wire and thermocouple arrangement is shown in Fig. 2. Thermocouples *A*, *B*, and *C* were placed in contact with the cotton-wrapped 30-gauge constantan heater. The leads from these thermocouples were kept in contact

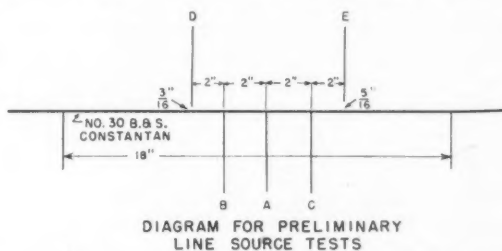DIAGRAM FOR PRELIMINARY
LINE SOURCE TESTS

FIG. 2. Thermocouple and heater arrangement for preliminary tests.

with the heater wire for about $\frac{1}{2}$ in. before being brought out through the sample, to minimize heat conduction away from the thermocouple junctions. Thermocouples *D* and *E* were not in contact with the heater, and their leads were brought straight out of the sample.

2. *Tests with Probes*

A number of probes tested in insulating materials (3, 4) had given results which were generally unsatisfactory. It was decided therefore to try out a number of modifications of a probe made from the smallest diameter tubing available. Aluminum tubing was used because of its high thermal conductivity, and availability in a range of sizes.

The same rock wool insulation previously described was used in these tests.

3. *Tests of Effect of Heater Current and Orientation*

This series of tests was made with unenclosed wire heaters to determine how the calculated value of *k* varied with heat flow rate, and to determine the effect of heater orientation. Tests were made with the heater horizontal and with the heater vertical, at three widely separated values of *q*. A 24 gauge (.02 in. diameter) heater was used in all the tests. A single thermocouple was located in contact with the heater at its mid-point. The thermocouple leads ran in opposite directions along the heater and in contact with it, to minimize the effect of heat loss at the thermocouple junction. Granulated rock wool at a density of 10 lb. per cu. ft. was used.

4. Tests Using Various Insulations

This series of tests was made with unenclosed wire heaters to determine their performance in various kinds of insulation. Four tests were made with granulated rock wool at a density of 10 lb. per cu. ft., two with a 24 gauge heater, and two with a 30 gauge heater; blanket rock wool was tested at four densities with a 24 gauge heater and at two densities with a 30 gauge heater; silica aero-gel was tested at 8 lb. per cu. ft. with a 24 gauge heater, and slab cork (density 10 lb. per cu. ft.) with a 30 gauge heater.

A single 30 gauge thermocouple with its leads taken out of the sample along the heater was used in all the tests.

RESULTS AND DISCUSSION

1. Preliminary Tests

Table I summarizes the results from this series of tests. The values of k are all much too high and indicate a serious error. Results given by thermocouple A, in the center (Fig. 2), gave higher values of k than did the outside thermocouples B and C. The latter gave quite similar results. This comparison indicates that the error was caused by heat conduction through the thermocouple leads. Thermocouple A was affected not only by conduction through its own lead but by conduction along the heater and through the leads of B and C. Heat conduction away from the junction through a thermocouple lead decreases the temperature rise in the immediate vicinity of the thermocouple. This decreases $(\theta_2 - \theta_1)$ for any given period of time, thus increasing the calculated value of k.

The value of k given by thermocouple D, which was located 3/16 in. away from the heater, is almost as high as that given by thermocouple A. Evidently in this case the effect of heat conduction along the thermocouple lead was not reduced by conduction to the thermocouple along the heater wire.

Since the effect of thermocouple heat conduction was different for each thermocouple, results for different locations do not show the variation due to thermocouple position alone. A comparison of the several values given by thermocouple A does give some indication of the reproducibility of results. The maximum deviation from the mean is a little over 2%. The range of values within tests for different t's is as high as 4%. This variation shows the necessity of taking the average of a number of calculations in determining the results for any single test.

2. Tests with Probes

The results obtained in this series of tests are shown in Table II and Figs. 3, B; 3, C; and 4.

The values of k in Table II show that heat loss through the end leads of the probe increases the calculated value of k, that even two 30 gauge (.01 in. diameter) copper wires make an appreciable difference in heat loss through leads, and that when the end loss approaches negligible proportions, as it does in tests 3(a), (b), (c), (d), and 6(a), the value of k given by the probe is between 10 and 15% lower than accepted hot plate values. This point will be discussed subsequently.

TABLE I

PRELIMINARY TESTS

(Test sample: granulated rock wool. Density, 10 lb./cu. ft. Hot plate conductivity, .27–.28. Heater No. 30 B & S constantan.
Thermocouples No. 30 B & S copper-constantan)

Test No.	Thermocouple No. *	k, B.t.u./sq. ft./hr./°F./in.	Base temp., °F.	Temp. rise, °F.	q, B.t.u./hr./ft.	t_0, sec.	k', corr. to 75°F. base temp. ***	Range, ** %	Diff. from mean of A, %
1(a)	A	.413	81	26	1.562	0	.408	3	+1.2
(b)	A	.406	75	26	1.565	0	.406	2	+0.7
(c)	A	.407	77	26	1.568	0	.405	4	+0.5
(d)	A	.392	72	23	1.418	0	.394	3	−2.2
(e)	B	.374	77	26	1.552	0	.372	3	
(f)	C	.367	74	26	1.548	0	.368	4	
(g)	C	.374	70	27	1.525	9	.378	4	
(h)	D	.388	66	26	1.548	−15	.395	3	

*See Fig. 2.
**Range of values of k calculated from different parts of the temperature–time curve, expressed as a percentage of the test average.
***This correction and the corresponding corrections in succeeding tables are based on work reported by Rowley, Jordan, and Lander (5).

TABLE II

TESTS WITH PROBES*

(Test sample: granulated rock wool. Density: 10 lb./cu. ft. conductivity, .27-.28)

Test No.	Probe No.	k, B.t.u./sq. ft./hr./°F./in.	Base temp., °F.	Temp. rise, °F.	q, B.t.u./hr./ft.	t_0, sec.	k', corr. to 75°F. base temp.	Range,** %
2(a)	A	.287	78	24	1.382	15	.285	4
(b)	A	.280	72	25	1.463	18	.282	4
(c)	A	.272	66	25	1.463	18	.280	2
(d)	A	.266	73	25	1.430	18	.268	6
3(a)	B	.252	79	25	1.250	48	.249	1
(b)	C	.255	79	24	1.250	39	.252	1
(c)	C	.258	74	25	1.250	45	.259	1
(d)	D	.248	77	24	1.250	45	.246	5
4(a)	E_1	.272	75	22	1.250	39	.272	5
(b)	E_1	.272	70	21	1.250	39	.276	5
5(a)	E_2	.257	71	21	1.062	39	.260	1
(b)	E_2	.262	76	21	1.062	42	.261	2
6(a)	E_3	.255	78	25	1.290	39	.253	1

*See Fig. 1, A for basic dimensions of the probe used in all tests. The following variations in construction were introduced into the different tests:

A—No. 14, B & S gauge copper power leads; two 30 B & S gauge thermocouples.

B, C, D—No. 24 B & S gauge copper power leads; two 30 B & S gauge thermocouples.

E_1—No. 24 B & S gauge copper power leads; two 30 B & S gauge thermocouples.

E_2—Same as E_1 except No. 30 B & S gauge copper power leads for second thermocouple cut off at end of probe.

E_3—Same as E_2 except No. 30 B & S gauge copper power leads.

**Range of values of k calculated from different parts of the temperature–time curve, expressed as a percentage of the test average.

Typical time–temperature rise curves for probes with 14 gauge and 24 gauge power leads (Figs. 3, B, 3, C) show that the time correction decreases with increasing heat loss through end leads, indicating a distortion of the whole curve.

Fig. 4 shows the time–temperature curves for Test 4(*a*) (temperature read from a thermocouple inside the probe) and test 4(*b*) (temperature read from a thermocouple in contact with the outside of the probe). The curves indicate that the thermocouple inside the probe was not at the same temperature as the aluminum tube, but that the temperature difference was relatively constant.
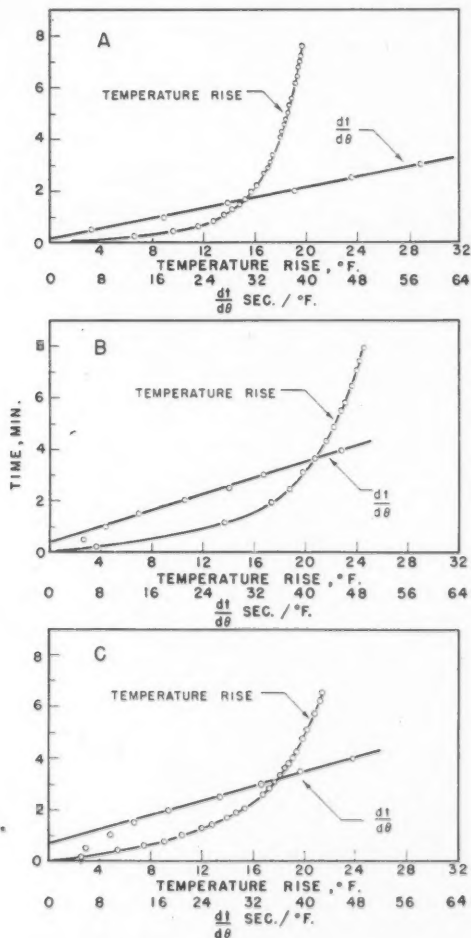

FIG. 3.   Typical temperature rise and $dt/d\theta$ curves for:
A, unenclosed heater,
B, probe with 14 gauge power leads,
C, probe with 24 gauge power leads.

Hence, the two tests gave approximately the same calculated value of k. It may be seen therefore, that the temperature drop between the heater wire and the outside of the probe apparently has little effect on the calculated value of k.
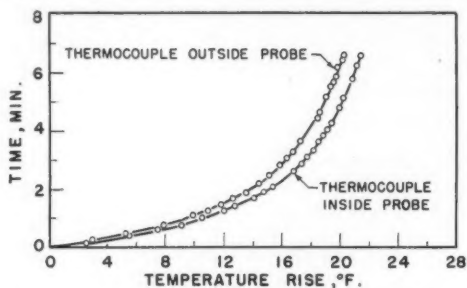
Fig. 4.   Temperature rise curves with thermocouple inside and outside probe.

3. *Effect of Heater Current and Position*

The results of this series of tests are shown in Table III and Fig. 5.

The tests showed that the calculated values of k increased with increased heat flow. In Fig. 5, B when the calculated k is plotted against the temperature
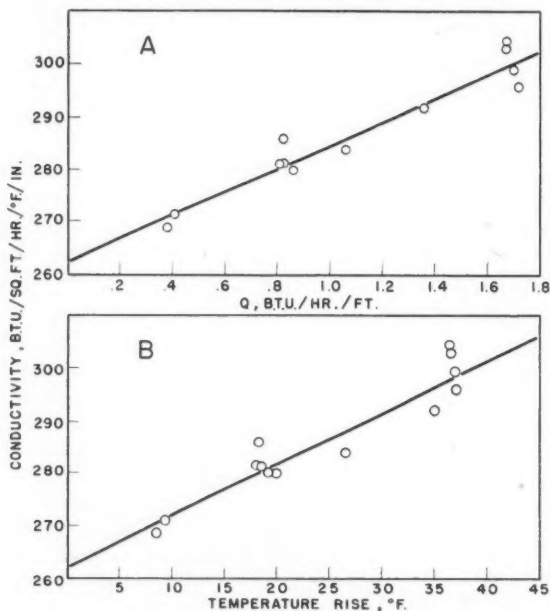

Fig. 5.   Variation in calculated conductivity with:
A, heat flow,
B, temperature rise.

TABLE III

Tests of Effect of Heater Current and Orientation

(Test sample: granulated rock wool. Density: 10 lb/cu. ft. Hot plate conductivity, .27-.28. Heater: No. 24 B & S gauge constantan. Thermocouple No. 30 B & S gauge copper–constantan, leads wrapped around heater)

Test No.	q, B.t.u./hr./ft.	Pos'n. horiz. or vert.	k, B.t.u./sq. ft./hr./°F./in.	Base temp., °F.	Temp. rise, °F.	t_0, sec.	k', corr. to 75°F. base temp.	Av.	Av. of each current range	Range,* %
5(a)	1.715	H	.297	76	40	12	.296	.298		4
(b)	1.700	H	.297	72	40	12	.299			2
6(a)	1.670	V	.301	73	38	9	.303	.303	.300	3
(b)	1.670	V	.301	71	40	9	.304			3
7(a)	0.822	H	.284	72	18	12	.286	.283		5
(b)	0.856	H	.278	73	19	9	.280			4
8(a)	0.818	V	.279	73	18	9	.281	.281	.282	6
(b)	0.815	V	.272	64	18	12	.281			5
9(a)	0.385	H	.269	75	9	9	.269			5
10(a)	0.409	V	.268	71	9	9	.271			6

*Range of values of k calculated from different parts of the temperature–time curve, expressed as a percentage of the test average.

rise during the test, the relationship appears to be linear. In Fig. 5, A the calculated k, plotted against heat flow, also gives a linear relationship. The conductivities were adjusted to a 75°F. base temperature for both plots. This phenomenon of change in apparent conductivity with heat, and hence with temperature rise, is presumed to be due to the actual change in conductivity of the test material with temperature change. The effect of heat flow by convection was considered negligible for reasons to be discussed below.

It should be noted that the "temperature rise at end of test" is not mean temperature, and that no actual mean temperature can readily be obtained for the transient conditions existing in these tests. However, it is evident that actual change in thermal conductivity can be related to either the temperature rise change of Fig. 5, B or the heat flow change of Fig. 5, A by plotting conductivity against mean temperature on the same graph. This would enable transient heat flow measurements at any rate of heat flow to be related to hot plate measurements at any mean temperature.

A comparison of the tests made with the heater horizontal and those with the heater vertical shows no significant difference, indicating that convective heat flow was of minor importance in these tests.

A point of speculative interest is the significance of the k value obtained by extrapolating the curve of Fig. 5, B to zero temperature rise, or the curve of Fig. 5, A to zero heat flow. Both give the same value, 0.263. This conductivity may be the actual conductivity, as opposed to the apparent conductivity measured in a sample having a conductivity gradient.

4. Tests Using Various Insulations

The results of this series of tests are shown in Table IV. The tests in granulated rock wool at 10 lb. per cu. ft. show that there are no appreciable differences between the 24 and 30 gauge heaters in this material. The t_0 correction is lower for the 30 gauge heater, but this is to be expected, since its cross-sectional area is only $\frac{1}{4}$ that of the 24 gauge heater.

Tests 13(a), (b), and (c), in which a 24 gauge heater was used in low density blanket type rock wool, are particularly interesting because of the similarity of the results to those of Tests (3), (4), (5), and (6), in which probes were tested in granulated rock wool at 10 lb. per cu. ft. The temperature and $dt/d\theta$ curves were similar to the one shown in Fig. 3, C. The k value for Test 13(a) varied between .227 and .390 depending on the values of t used, and t_0 was greater than 60 sec. No exact t_0 could be determined. In Tests 13(b) and (c), as the sample density was increased t_0 decreased. The value of k for 13(b) is a little low, but the value for 13(c) is satisfactory, considering the low current used.

The 30 gauge heater gave satisfactory results at both densities of the blanket type rock wool sample. A test could not be made at 1.8 lb. per cu. ft. with the 30 gauge heater because the sample had been permanently deformed during the higher density experiments.

A comparison of the results of Tests 13 and 14 with the results of the probe tests shows that, when the heater is too large in diameter or the sample density

TABLE IV

TESTS USING VARIOUS INSULATIONS

(Thermocouple: No. 30 B & S copper–constantan, leads wrapped around heater)

Test No.	Sample	Density, lb./cu. ft.	Hot plate	k, B.t.u./sq. ft./hr./°F./in.	Base temp., °F.	Temp. rise, °F.	q, B.t.u./hr./ft.	Heater size, B & S gauge	t_o, sec.	k', corr. to 75°F. base temp.	Range,*%
11(a)	Rock wool gran.	10	.27-.28	.297	76	40	1.715	24	12	.296	4
(b)	"	10	.27-.28	.284	72	18	0.822	24	12	.286	5
12(a)	"	10	.27-.28	.288	70	35	1.353	30	6	.292	3
(b)	"	10	.27-.28	.287	79	27	1.062	30	3	.284	3
13(a)	Rock wool blanket	1.8**	.27	.256	74	25	0.897	24	$t_o > 60$	.261	3
(b)	"	2.9	.27	.265	69	17	0.622	24	30	.266	3
(c)	"	4.0		.263	74	16	0.595	24	30	.265	3
(d)	"	8.7	.27	.269	73	14	0.600	30	12	.273	3
14(a)	"	3.7		.272	71	30	1.100	30	12	.273	2
(b)	"	8.7			74	28	1.100	30	12	.273	
15(a)	Silica aero-gel	8.0	.155	.155	74	29	0.915	24	9	.155	3
(b)	"	8.0	.155	.153	68	21	0.651	24	9	.155	3
16(a)	Slab cork	10.0	.300	.300	72	22	1.100	30	3	.301	3

*Range of values of k calculated from different parts of the temperature–time curve, expressed as a percentage of the test average.

**k for this test varied between .227 and .300 depending on the part of the curve over which it was calculated.

too low, the calculated value of k is low, and the t_0 correction large. The t_0 correction is an approximation. Graphs plotted in Van der Held's paper (6) show this, and it can be seen if Equation (3) is considered for small values of t. For t_0 to be correct for all values of t, the temperature rise of the heat source at $t = t_0$ would have to be zero, and this is obviously not so. It therefore appears that the error in k is related to an increasing error in t_0, as t_0 becomes greater.

CONCLUSIONS

The tests showed that the probe did not give satisfactory results in insulations. The reason appears to be the approximate nature of the correction made to allow for the finite size of the probe and the difference between thermal properties of the probe and those of the test sample. A different method of making this correction may increase the range of usefulness of the probe. It should be pointed out that these results indicate that the probe should give good results in at least some materials of greater density than those tested in this investigation, and previous experimental work (3, 4) shows that this is so, at least under some conditions.

On the other hand, the unenclosed heater gave good results in the insulations tested when a sufficiently small heater was used, and when care was taken to minimize heat conduction through the thermocouple leads. Although the unenclosed heat source cannot be used as conveniently as a probe, the transient heat flow method of conductivity measurement described does offer the previously mentioned advantages over the hot plate method.

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REFERENCES

1. HOOPER, F. C. and LEPPER, F R.   Heating, Piping Air Conditioning, 22(8) : 129-135. 1950.
2. INGERSOLL, L. R., ZOBEL, O. J., and INGERSOLL, A. C.   Heat conduction. McGraw-Hill Book Co. Inc., New York. 1948.
3. LEPPER, F. R.   M.A.Sc. Thesis.   University of Toronto. 1950.
4. MASSON, G. R.   M.A.Sc. Thesis.   University of Toronto. 1950.
5. ROWLEY, F. B., JORDAN, R. C., and LANDER, R. M.   Refrig. Eng. 50(8) : 541-544. 1945.
6. VAN DER HELD, E. F. M. and VAN DRUNEN, F. G.   Physica, 15(10) : 865-881. 1949.

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